Investigation of local degradation effects

M. Schulze, A. Haug, E. Gülzow, K.A. Friedrich
Deutsches Zentrum für Luft- und Raumfahrt (DLR)
Institut für Technische Thermodynamik
Pfaffenwaldring 38-40
D-70569 Stuttgart, Germany

Introduction

The lifetime of polymer electrolyte fuel cells (PEFC) is insufficient for many applications. Therefore, the investigation and understanding of the degradation processes is essential for increasing lifetime. In order to understand the degradation processes it is necessary to investigate not only the integral behaviour as function of time, but also local effects. For these investigations in-situ methods like current density distribution and electroche-mical impedance spectroscopy measurement as well as ex-situ methods like scanning electron microscopy and X-ray photoelectron spectroscopy have been applied. The in-situ methods allow the quantification of the effect of the degradation, whereas the ex-situ methods allow the identification of the degradation processes.

Methods

At the German Aerospace Center (DLR) U(i)-characteristics, chronopotentometry, electrochemical impedance spectroscopy and current density distribution measurement are used to investigate the degradation processes during the fuel cell operation. For the current density distribution measurement a printed circuit board (PCB) technique will be used [1]. In contrast to the other in-situ methods the current density measurement provides locally resolved information about the local performance.
For the identification of the degradation processes various methods are used at the DLR; the scanning electron microscopy yields information about the struc-ture and structural changes, the X-ray photoelectron spectroscopy provides information about the chemical composition of the surfaces and their alterations induced by the degradation.
For the investigation of the degradation processes a single cell with 50x50 mm^2 were used; the printed circuit board for the current density measurements has 49 segments each 7x7 mm^2.

Results and Discussion

Fig. 1 shows the cell voltage during a constant galvanostatic operation. The cell voltage decreases with time. At the marked interrupts the cell was dried. After this drying procedure the fuel cell operation was restarted with the same applied load as before. It can be clearly seen, the cell performance is significantly recovered after the drying procedure, but the following decrease is accelerated. In addition, also the maximum performance after the drying cycles decrease. This behaviour indicates at least two different degradation processes:

(i) loss of the maximum performance (irreversible losses) after the drying step
(ii) the performance loss, which can be recovered by the drying processes.

The second one is called “reversible“ loss. However, the accelerated performance loss after the drying steps indicates, that this degradation process is also related to an irreversible alteration in the fuel cell, which can be compensated by adaption of the operating conditions.
The degradation inside the fuel cell is not a homogenous process over the complete active area as shown in the alteration of the current density distribution due to operating time. The Fig. 2 and 3 show the current density distributions measured for a new cell and after approx. 400 h at constant cell voltage (600 mV). Besides the decrease of performance, the current density distribution was significantly changed. It can be clearly seen that the area with high performance becomes smaller, and in addition, the area shifts to he lower right region. The area with low performance increases significantly. The alteration of the current density distribution and the related local performance losses marks the areas with a more significant degradation.

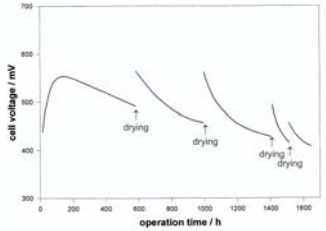

Fig. 1: Alteration of the cell voltage of a PEFC single cell during constant galvanostatic loading in a long-term experiment

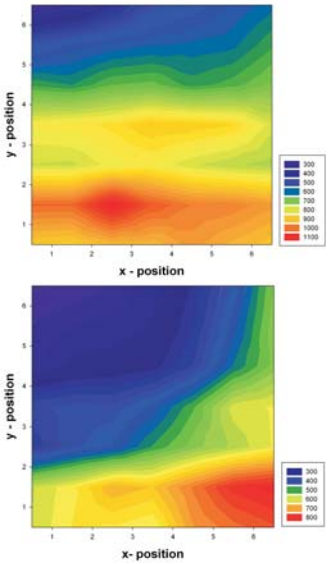

Fig. 2: Current density distribution in a new single cell (on top) and after an operating period of approx. 400 h at 600 mV (bottom).

Using electrochemical impedance spectrometry the “irreversible“ and “reversible“ losses were quantified for anode and cathode separately. For the evaluation of the impedance spectra the equivalent circuit shown in Fig. 4 was used. Using the change of the transfer resistances of the anode and the cathode the irreversible and reversible losses were distinguished (Table 1).

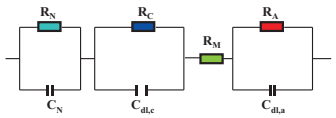

Fig. 3: Equivalent circuit for the evaluation of the electrochemical impedance spectra

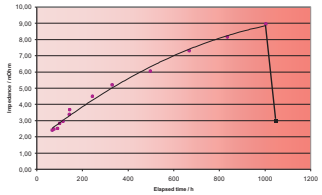

Fig. 4: Variation of the transfer resistance related to the anode reaction derived from the impedance measurement)

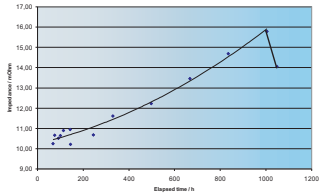

Fig. 5: Variation of the transfer resistance related to the cathode reaction derived from the impedance measurement

	Anode	Cathode	Sum
Reversible degradation after 1000 h	**68.8 mV**	**20.0 mV**	**88.8 mV**
Irreversible degradation after 1000 h	**5.4 mV**	**43.2 mV**	**48.6 mV**
Degradation after 1000 h	**74.2 mV**	**63.2 mV**	**137.4 mV**

Table 1: Breakdown of voltage (performance) losses resulting from long-term operation into reversible and irreversible degradation after evaluation of EIS determined after 1000 h of operation

In addition to the in-situ measurements the fuel cell components were also characterized before and after operation. In contrast to the electrochemical in-situ methods this ex-situ characterization is typically locally resolved. For these ex-situ investigations small samples were selected from the area, which allow a local analysis the fuel cell components. In addition, the separation of the different fuel cell components enables a vertical resolution.

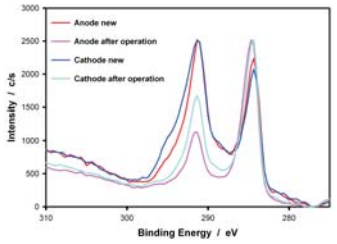

Fig. 6: C1 s spectra (XPS) of a new and an unused CCM

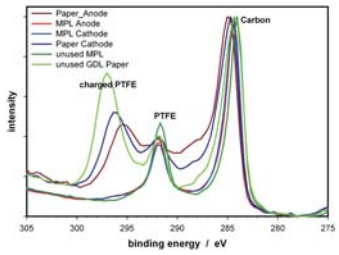

Fig.7: C1 s spectra (XPS) of new and used GDL

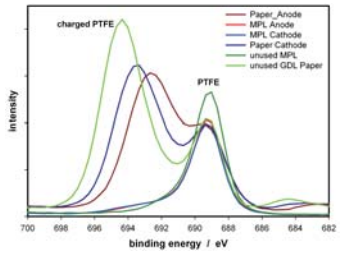

Fig. 8: F1 s spectra (XPS) of new and used GDL

The degradation of PTFE in the electrode and in the GDL [3] were investigated by X-ray photoelectron spectroscopy. For both components, a partially decomposition of the PTFE can be observed. The decomposition of the PTFE is more significant on the anode side than on the cathode side. These investigations show also that the PTFE decomposition is not only an effect on the surface of one component, it takes place over the complete thickness of the electrode (reaction layer + GDL). Caused by the decomposition of the PTFE the water balance in the cell is changed and induces the “reversible“ degradation effect shown in Fig. 1. The reversible degradation is related to the platinum agglomeration [4] as shown in Fig. 9-14. In areas, which are flooded by liquid water the agglomeration and mobility of the platinum is enhanced.

Fig. 9: Reaction layer of a new electrode

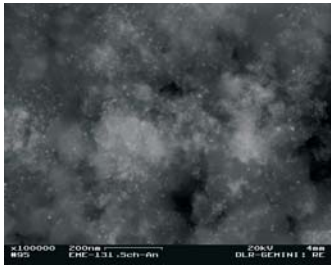

Fig. 10: Reaction layer of an used anode

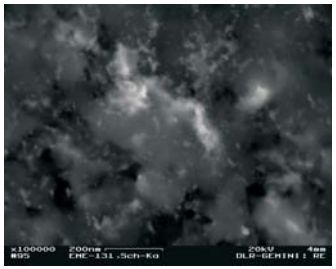

Fig. 11: Reaction layer of an used cathode

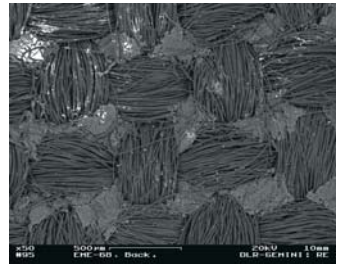

Fig. 12: Backside of the cathodic GDL in area, which was flooded by liquid water, after fuel cell operation

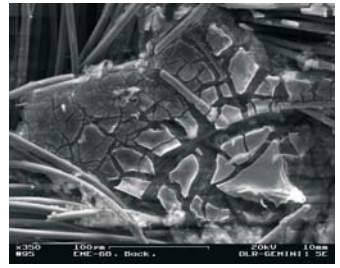

Fig. 13: Backside of the cathodic GDL in area, which was flooded by liquid water, after fuel cell operation, higher magification

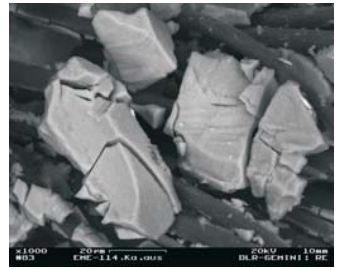

Fig. 14: Backside of the cathodic GDL in area, which was flooded by liquid water, after fuel cell operation

References
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